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THE POLYMERIZATION OF ACROLEIN AND ITS DERIVATIVES

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1. The Low-Temperature Polymerization of Acrolein
and α -Methylacrolein

I. V. Andreyev, M. M. Koton and K. A. Kovalev

ABSTRACT

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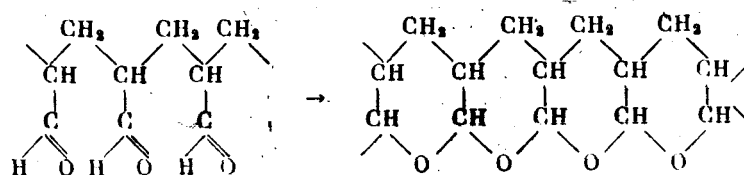
Low temperature polymerization of acrolein and derivatives under various conditions and resultant polymers were studied. It was established that α -methylacrolein is polymerized more slowly than acrolein.

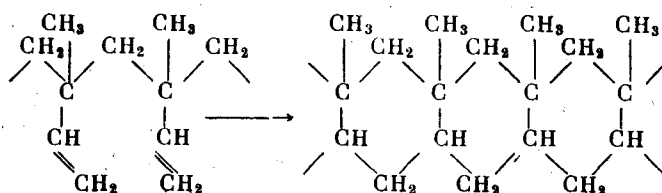
The polymerization of acrolein and the study of the structure and properties of acrolein polymers are currently attracting a great deal of attention on the part of researchers. Large scale investigations in the field of the polymerization of acrolein, studies of its polymer structure and the modification of polyacrolein properties are being carried out by Kern and his associates (refs. 1-3). They made a study of acrolein polymerization in the presence of various catalyzers. Thus they studied the polymerization of acrolein in block in the presence of boron trifluoride etherate from 0° to $+20^{\circ}$. Polyacroleins containing 15-20 percent aldehyde groups are formed in this condition.

This study deals with the polymerization of acrolein and α -methylacrolein by gaseous BF_3 , in block and in solution, at temperatures ranging from 0° to

*Numbers given in the margin indicate the pagination in the original foreign text.

-80°. In the case of the block polymerization of acrolein, the BF_3 was used both in the absence of moisture and oxygen in the air and with water especially added as catalyzer. The presence of traces of moisture leads to a sharp increase in the rate of acrolein polarization. Thus if a 15-20 percent conversion of an acrolein monomer to a polymer at -20° in "ideal" conditions required 15-30 hours, a similar conversion in the presence of traces of water, with all other conditions being equal, took place in 3-8 hours. The decrease in the molecular weight of the polyacrolein observable in the latter case is indicative of the difference in the growth mechanism and the break of the chain. In addition to the changing polymerization conditions, the polymer properties are considerably affected by the depth of the polymerization and the residual quantities of the catalyzer. The degree of acrolein polymerization in block is highest at temperatures between -20° and -40° with the BF_3 content in the reaction mixture amounting to 1.5 molecular percent, and in the case of α -methylacrolein with a BF_3 content equaling 2.5-3 mol percent. Free aldehyde groups are not found in the vitreous polyacrolein obtained in these conditions, apparently because the aldehyde group plays an active part in the polymerization reaction. Polyacrolein is insoluble in organic solvents but soluble in sulfurous acid. It is quite probable that the polymerization of acrolein in the conditions under study takes place in a "head to tail" position whereby all the aldehyde groups are located on one side of the basic chain, and this facilitates the formation of a vitreous polymer with a cyclic-structure chain consisting of condensed six-membered oxygen-containing links:





The cyclized polyisoprene produced in these conditions is a vitreous polymer with a high thermal stability.

The Experimental Aspect

Acrolein polymerization. The polymerization reaction was carried out in sealed ampoules. The instrument with the ampoules and measuring tanks were vacuumized three times and each time washed with dry pure nitrogen. Tubular heating devices are fitted over ampoules 3 and measuring tank 2, heated to 300-350° and the system then vacuumized (Fig. 1). The traces of moisture and the occluded oxygen are removed from the ampoules.

After 1.5-2 hours of heating, the heaters are removed and the ampoules closed. A monomer is then introduced into tank 2 in a nitrogen flow. The nitrogen above the monomer which contains some oxygen that had gotten into it when the tank was being filled, is removed by a vacuum-cooling process and the tank is then washed with nitrogen.

After the instrument has been washed with nitrogen three times and a vacuum (0.5 mm) produced in it, the monomer is distilled from the measuring tank into the ampoule. The distillation is made possible by the good vacuum and the cooling of the ampoules (-80°) while the cooling of the measuring tank is discontinued. The ampoules are then closed. The instrument is filled with nitrogen, and its right part is removed from section 1 and replaced with a burette containing gaseous boron trifluoride (ref. 5). Just as at the time

measuring tank 2 was connected with the monomer, the entire instrument is vacuumized three times and each time filled with nitrogen.

The next step is to introduce the necessary quantity of gaseous boron trifluoride through the instrument into each ampoule in the vacuum (0.5 mm). /530

Cooled with liquid nitrogen and filled with a frozen monomer and catalyzer, the ampoules are unsoldered and transferred to a Dewar flask or another cryostat with a temperature suitable for polymerization purposes.

Refining and drying the monomers. The reactive acrolein was dried with calcium chloride and in a nitrogen current under atmospheric pressure and distilled in a column. The fraction with a melting point of 52-53° was removed. This acrolein fraction was then dried again, and distilled in a special instrument at room temperature under 1-2 mm nitrogen pressure in order to avoid the polymerization-connected losses.

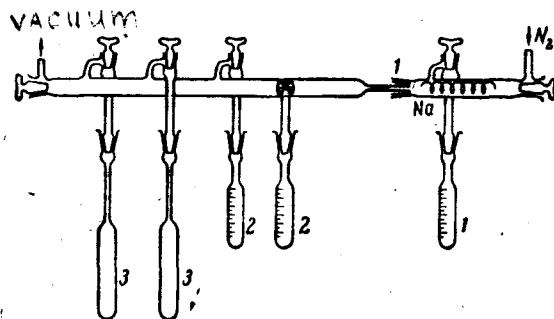


Figure 1. Ampoule-filling apparatus

The α -methylacrolein yield was 70 percent. The conditions we selected for the synthesis are described in Green's study (ref. 6). The resulting monomer was dried with calcium chloride and distilled at 62-63°. It was additionally dried with phosphoric pentoxide and cooled with ice. In a following distillation, the α -methylacrolein was effectively distilled at 28.5-29° under a residual pressure of 145 mm.

After drying it with calcium chloride, α -ethylacrolein (ref. 7) can be distilled in a column without the use of hydroquinone. Almost all of it is converted at 91-92°. It was dried a second time with phosphoric pentoxide, as indicated for α -methylacrolein, and purified by distillation in a good vacuum (0.5 mm) at room temperature.

Investigating the polymer. Before analyzing the initiator, the polymer was processed by the following method: the ampoule was opened at the same temperature at which the polymerization had taken place and connected to a vacuum pump through a system of traps (Fig. 2). This eliminated the excessive gaseous boron trifluoride which condensed and froze in trap 3.

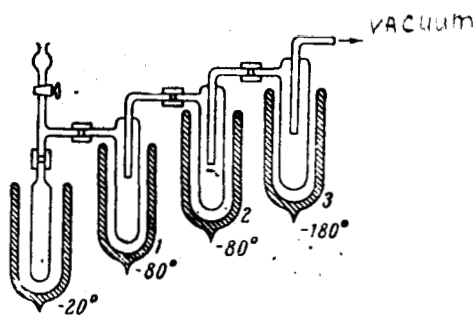


Figure 2. Polymer-isolating device

Thereafter, if the reaction mixture is still mobile, the monomer is distilled off from it and condensed in trap 1. After the excessive catalyzer mass and the possible monomer quantities have been removed, a solvent is added to the reaction mixture and the vacuum process continued. The catalyzer and monomer continue to be extracted from the reaction mixture in this process. Ether is then introduced in small portions for the complete removal of the boron trifluoride. The activity of the catalyzer is thereby sharply reduced, as a result of its conversion to boron trifluoride etherate. 0.5-1 milliliter of methyl alcohol is then introduced with the ether. After such a treatment the

polymer, if it is soluble, is precipitated as ether or h-hexsane. If the polymer is insoluble, it is washed with ether a number of times. The polymer was finally treated with ether in a Soxhlet apparatus; such treatment, under relatively mild conditions, leads to the elimination from the polymer of the boron trifluoride etherate and the monomer which combines with solid alkali. Without such a treatment the polymer will in time grow dark and change its properties.

Cited in Fig. 3a are the data on the rate of acrolein and methylacrolein polymerization in block at -20° in the presence of gaseous boron trifluoride and in the complete absence of moisture and oxygen.

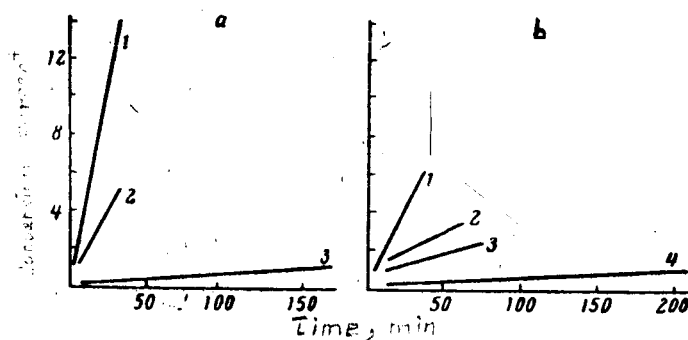


Figure 3. The acrolein and α -methylacrolein polymerization rate: a-in block, b-in solution.

a: 1-acrolein in block, 3 mol percent BF_3 ;

2-acrolein in block, 2.5 mol percent BF_3 ;

3- α -methylacrolein in block, 5.0 percent, BF_3 ;

b: 1-acrolein in block, 2.5 mol percent BF_3 ;

2, 3, 4-acrolein in a 15, 14 and 7 molarity solution, 2.5 mol percent BF_3 .

It follows from Fig. 3 a that if a 2 percent conversion of a-methylacrolein to a polymer in the presence of 5 mol. percent BF_3 requires 4-5 hours, the polymerization of a-ethylacrolein under the same conditions would take dozens of hours which could not be reflected in this graph.

Fig. 3 b shows the rate of acrolein polymerization in the presence of gaseous boron trifluoride at -20° in a CH_2Cl_2 solution.

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Listed in the table are the comparative figures on the acrolein polymers produced by a 25-30 percent conversion under various conditions.

The block polymerization of acrolein in the complete absence of moisture and oxygen results in the development of more high molecular products in its soluble portion (see table). Fully soluble polymers can be produced by a 13-15 percent conversion; in the case of a 25-30 percent conversion (see table), such polymers are, as a rule, insoluble in organic solvents. Soluble polyacroleins eventually lose some of their solubility in organic solvents, but are soluble in sulfurous acid.

THE POLYMERIZATION OF ACROLEIN IN THE PRESENCE OF GASEOUS
BORON TRIFLUORIDE UNDER VARIOUS CONDITIONS (AT -20°)

Conditions			Results		
Polymerization	Cocatalyzer	Polymerization time hours	Solubility in organic solvents, %	(η)	Melting point, $^\circ\text{C}$
In block	None	15-30	10	0.12-0.17	270-320, decompos.
In block	H_2O	3-8	15	0.07-0.08	270-300, decompos.
In solution	CH_2Cl_2	20-35	100	0.06-0.07	140-170

Analysis of the insoluble portion of the polyacroleins, obtained in a block by a 30 percent (and higher) conversion in the complete absence of moisture and oxygen, revealed an absence of oximes of aldehydes (ref. 8). Phenylhydrazone could not be obtained from a polyacrolein water solution after it had been dissolved in sulfurous acid. But in the soluble portion of the polymer obtained in these conditions from α -methylacrolein, 9 percent aldehyde groups were found by the oximation method, which revealed no aldehyde groups in the insoluble polyacrolein polymerized by a 40 percent conversion in a methylene chloride solution.

Polymers with a melting point of 140-170° and (η) 0.06-0.07 were obtained /532
from the polymerization of acrolein in a solution by a 25-30 percent conversion.

It would be interesting to point out that insoluble vitreous poly- α -methylacrolein, unlike polyacrolein, is converted to powder if treated with solvents.

The thermal stability of polyacrolein and poly- α -methylacrolein has been investigated; as indicated in Fig. 4, the α -methylacrolein polymers have a higher thermal stability than do the acrolein polymers.

According to preliminary data, the α -ethylacrolein polymer, obtained in a block in the presence of gaseous boron trifluoride, has (η) 0.065 (benzene) and a relatively high melting point.

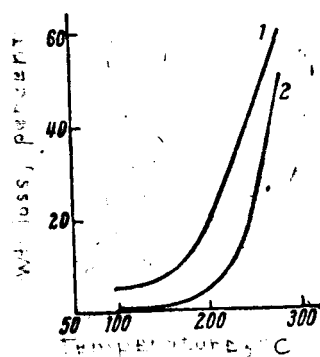


Figure 4. The thermal stability of polymers:

1-polyacrolein, 2-poly- α -methylacrolein.

Conclusions

1. The low-temperature polymerization of acrolein and a-methylacrolein with gaseous boron trifluoride, in block and solution has been studied.
2. It has been established that the block-polymerized acrolein forms primarily polymers which are insoluble in organic solvents and soluble in sulfuric acid; such polymers do not contain any free aldehyde groups.
3. A study has been made of the acrolein and a-methylacrolein polymerization rate at -20° in the presence of gaseous BF_3 . It has been established that a-methylacrolein is polymerized at a slower rate than acrolein.
4. An a-ethylacrolein polymer has been obtained.

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